

Process for the preparation of polymerides of vinyl chloride

The subject-matter of the invention is a process for the preparation of homo-, co- or graft copolymerides of vinyl chloride by means of polymerisation of vinyl chloride alone or with up to 30 wt.%, calculated on used vinyl chloride, of at least one monomer which is copolymerisable with vinyl chloride and/or at least one polymer which is graft-copolymerisable with vinyl chloride, in aqueous suspension or in mass in the presence of at least two peroxide groups-containing catalysts, one of which is cumyl perneodecanoate.

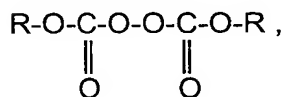
The polymerisation of vinyl chloride proceeds according to a radical mechanism. To start the polymerisation reaction, operation generally is in the presence of radical-forming substances, which act as catalyst, in particular such substances as contain peroxide groups.

In so far as the polymerisation is carried out in aqueous suspension in the presence of a suspension stabiliser (protective colloid) or in the mass, oil-soluble catalysts are used, i.e. such catalysts as are soluble in the used monomers or mixture of monomers. A survey of older known processes is to be found for instance in the book *Polyvinylchlorid und vinylchlorid-Mischpolymeride* of H. Kainer; Springer Verlag, 1965, pages 7, 8, 12 as well as 16 to 25.

Further, it is known, for instance from the book by Harold A. Sarvetnick, *Polyvinyl Chloride* van Nostrand Reinhold Company / New York (1969), page 42, that for instance in a typical suspension polymerisation of vinyl chloride toward the end of the polymerisation time there is a rise in the conversion rate and hence in the quantity of heat developed. Since the properties of the obtained polymers are dependent on the polymerisation temperature, this is generally kept constant during the polymerisation, that is to say, toward the end of the polymerisation a disproportionately high cooling capacity must be available in order to reach constancy of temperature, in particular when on economic grounds operation has to be with high throughputs and short times until the end of the polymerisation. To obviate this drawback it is known from

DE-OS 19 15 386 to carry out the suspension polymerisation of vinyl chloride in the presence of an initiator (catalyst) mixture of acetylcyclohexane sulfonylperoxide and either tert.-butyl perpivalate or di-isopropyl percarbonate. In this way a more even distribution of the heat emission during the polymerisation is indeed achieved, albeit accepting significant polymer coatings on the reactor walls, as Comparative experiment B detailed below shows. These wall coatings are undesired, since they make the passage of heat from the polymerisation mixture to the reactor wall more difficult, and with that reduce the cooling performance of the reactor and moreover contaminate the formed polymeride with coarse components when parts of this coating detach themselves from the wall during the polymerisation, which happens time and again.

From DE-OS 21 39 680 it is further known to polymerise vinyl chloride in aqueous suspension in the presence of two oil-soluble radical-forming catalysts, one of which is either acetylcyclohexane sulfonylperoxide or lauroyl peroxide while the other is a percarbonate of the formula



wherein R can mean a branched or linear alkyl radical with 10 to 20 carbon atoms, a cycloalkyl radical or aryl radical with 6 to 14 carbon atoms substituted or unsubstituted with alkyl radicals containing 1 to 4 carbon atoms. According to the explanations in the document, the catalyst mixture is used to achieve an improvement of the property of the obtained polymer. As is shown by Comparative experiment C detailed below, the catalyst mixture is also suited for obtaining a more even heating pattern during the polymerisation, though likewise accepting coating formation on the reactor walls.

A process has now been found which does not have the drawbacks of the above-described processes and which allows operation with short operating times and balanced heat emission during the polymerisation, with an essentially lower coating formation being determined on the reactor walls. The new process for the preparation of homo-, co- or graft copolymerides of vinyl chloride by means of polymerisation of

vinyl chloride alone or with up to 30 wt.%, calculated on used vinyl chloride, of at least one monomer which is copolymerisable with vinyl chloride and/or at least one polymer which is graft-copolymerisable with vinyl chloride, in aqueous suspension or in mass at 30 to 80°C in the presence of at least two oil-soluble, radical-forming
5 peroxide groups-containing catalysts, as well as optionally in the presence of suspending agents and further additions, is characterised in that as catalysts are used

0.001 to 0.5 wt.%, calculated on used monomers, of cumyl perneodecanoate, and
0.001 to 0.5 wt.%, calculated on used monomers, of at least one further peroxide
10 groups-containing catalyst known for the polymerisation of vinyl chloride, which has a 1-hour-half life temperature of 50 to about 100°C.

The 1-hour half-life temperature is the temperature at which the respective catalyst within one hour contains only half of the original peroxide groups. Examples of
15 peroxide groups-containing catalysts known for the polymerisation of vinyl chloride which have a 1-hour-half life temperature of 50 to about 100°C are: dilauroyl peroxide; o,o'-methylbenzoyl peroxide; o,o'-dimethoxybenzoyl peroxide; t-butyl perpivalate; t-butyl perneodecanoate; t-amyl perneodecanoate; di-isopropyl peroxydicarbonate. Preferably use is made of peroxydicarbonates containing 14 to about 40
20 carbon atoms, since these in connection with cumyl perneodecanoate give particularly low wall coating formation. Examples of such peroxydicarbonates are: di-2-ethylhexyl peroxydicarbonate; dicyclohexyl peroxydicarbonate; dibenzyl peroxydicarbonate; di-cetyl peroxydicarbonate, and dimyristil peroxydicarbonate. Particularly favourable results are obtained with bis-(4-t-butyl cyclohexyl)-peroxy-
25 dicarbonate.

In the presence of less than 0.001 wt.%, calculated on used monomers, of cumyl perneodecanoate the effect according to the invention is no longer observed. The same holds when there is operation in the presence of less than 0.001 wt.%,
30 calculated on used monomers, of at least one further peroxide groups-containing catalyst known for the polymerisation of vinyl chloride with a 1-hour half-life temperature of 50 to about 100°C. Above 0.5 wt.%, calculated on used monomers, of

cumyl perneodecanoate the polymerisation reaction becomes more difficult to control and in general requires an unnecessarily high cost for cooling. Something similar holds when more than 0.5 wt.%, calculated on used monomers, of at least one peroxide groups-containing catalyst described in greater detail above is used.

- 5 Advantageously the charge amount of cumyl perneodecanoate, like that of the further catalyst known for the polymerisation of vinyl chloride is in the range of 0.01 to 0.1 wt.%, calculated on used monomers. In selecting the catalyst amounts it is expedient to take into account the molecular weight of the used catalyst, or its content of active peroxide groups. The higher the molecular weight and the lower the content of active
- 10 peroxide groups, the more of the catalyst in question is expediently used.

The catalyst used besides cumyl perneodecanoate can also be a mixture of several compounds. Additions of catalysts known for the polymerisation of vinyl chloride which do not contain peroxide groups, for instance azo compounds, are possible.

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The overall amount of used catalysts expediently should not be less than 0.01 wt.%, calculated on used monomers, since below this value the polymerisation generally proceeds too slowly.

- 20 Nor should the overall amount be selected above 0.5 wt.%, calculated on used monomers, since above this value the polymerisation often becomes more difficult to control. Especially good results are obtained in the range of 0.05 to 0.2 wt.%, calculated on used monomers, of overall amounts of used catalysts.

- 25 The catalysts are added to the polymerisation mixture either as such in finely powdered form or expediently in solution, for instance in monomers or aliphatic hydrocarbons, optionally with use of plasticisers known for polyvinyl chloride, or in dispersion, for instance dispersed in water.

- 30 In a gradual (batchwise) polymerisation, the addition generally takes place at the start of the polymerisation. Certain components may also be added subsequently. In a continuous polymerisation, the addition of the catalyst takes place continuously to

the same extent as the injection of the monomers into the polymerisation mixture. Here again the addition of part of the catalyst locally beyond the starting place of the polymerisation is possible.

5 The process according to the invention is suitable for polymerisation in mass and in particular for polymerisation in aqueous suspension. In this process up to 30 wt.%, calculated on used vinyl chloride, of at least one monomer which is copolymerisable with vinyl chloride and/or of at least one polymer which is graft-copolymerisable with vinyl chloride can be added. Preferably, up to 15 wt.%, calculated on used vinyl
10 chloride, of copolymerisable monomers and/or graft-copolymerisable polymers are used. In particular, the new process can also be used for the homopolymerisation of vinyl chloride.

For copolymerisation with vinyl chloride, for instance one or more of the following
15 monomers are suitable: olefins, such as ethylene or propylene, vinyl esters of linear or branched carboxylic acids with 2 to 20, preferably 2 to 4 carbon atoms, such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl 2-ethylhexoate, vinyl isotridecanoic acid ester; vinyl halides, such as vinyl fluoride, vinylidene fluoride, vinylidene chloride, vinyl ether, vinyl pyridine, unsaturated acids, such as maleic,
20 fumaric, acrylic, methacrylic acid and the mono- or diesters thereof with mono- or dialcohols with 1 to 10 carbon atoms; maleic anhydride; maleic acid imide, as well as the N-substitution products thereof with aromatic, cycloaliphatic, as well as optionally branched, aliphatic substitutions; acrylonitrile, styrene.

25 For graft copolymerisation, for instance cross-linked or uncross-linked elastomeric polymerides can be used which are obtained by polymerisation of one or more of the following monomers: dienes, such as butadiene, cyclopentadiene; olefins, such as ethylene, propylene; styrene, unsaturated acids, such as acrylic or methacrylic acid, as well as the esters thereof with mono- or dialcohols with 1 to 10 carbon atoms,
30 acrylonitrile, vinyl compounds, such as vinyl esters of linear or branched carboxylic acids with 2 to 20, preferably 2 to 4 carbon atoms, vinyl halides, such as vinylidene chloride and vinyl chloride. Said last, however, only with at least one of the

aforementioned monomers. Polymers to be grafted are expediently respectively dissolved in the monomers or used in the form of a dispersion.

The polymerisation can also be carried out using a pre- or seed polymeride.

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In particular in the case of polymerisation in aqueous suspension operation is in the presence of 0.01 to 1 wt.%, preferably 0.05 to 0.3 wt.%, calculated on used monomers, of one or more suspension stabilisers (protective colloids). To this end the suspension stabilisers known for the polymerisation of vinyl chloride are suitable, for instance cellulose derivatives, such as cellulose ethers, cellulose esters, cellulose amides; gelatins; polyvinyl alcohol; mixed polymerides of maleic acid or the half esters thereof with styrenes; mixed polymerides of vinyl acetate with N-vinyl acylamides, for instance N-vinyl-N-methyl-acetamide, or with N-vinyl pyrrolidone(2). Preferably, cellulose ethers, for instance methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, methylhydroxypropyl cellulose and/or partially acetylated polyvinyl alcohols with up to 50 mol.% acetate groups are used.

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Moreover, the polymerisation can be carried out in the presence of 0.01 to 1 wt.%, calculated on monomers, of one or more emulsifiers, in which case the emulsifiers can be used both for pre-emulsification of the monomers alone and also in the actual polymerisation in admixture with the above-mentioned suspending agents.

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The emulsifiers used can be anionic, amphoteric, cationic as well as non-ionic. Suitable as anionic emulsifiers are for instance alkali, alkaline earth, ammonium salts of fatty acids, such as lauric, palmitic or stearic acid, of acidic phosphoric acid alkyl esters, such as diethylhexyl phosphoric acid, of acidic fatty alcohol sulphuric acid esters, of paraffinic sulfoacids, of alkylaryl sulfoacids, such as dodecyl benzene or dibutyl naphthalene sulfoacid, of sulfosuccinic acid dialkyl esters, as well as the alkali and ammonium salts of epoxy groups-containing fatty acids, such as epoxystearic acid, of reaction products of peracids, for instance peracetic acid with unsaturated fatty acids, such as oleic or linoleic acid or unsaturated oxyfatty acids, such as ricinoleic acid. As amphoteric or cation-active emulsifiers are suitable for instance:

alkyl betaines, such as dodecyl betaine, as well as alkyl pyridinium salts, such as lauryl pyridinium hydrochloride, also alkyl ammonium salts, such as oxethyldodecyl ammonium chloride. Suitable as non-ionic emulsifiers are for instance: partial fatty acid esters of polyvalent alcohols, such as glycerin monostearate, sorbitol monolaurate, sorbitol oleate or sorbitol palmitate, polyoxyethylene ethers of fatty alcohols or aromatic hydroxy compounds, polyoxyethylene esters of fatty acids, as well as polypropylene oxide-polyethylene oxide condensation products.

Besides catalysts, optionally protective colloids and/or emulsifiers, the polymerisation can be carried out in the presence of buffer substances, for instance alkali acetates, borax; alkali phosphates, alkali carbonates, ammonia, as well as means for controlling the molecule size, such as for instance aliphatic aldehydes with 2 to 4 carbon atoms, chlorinated hydrocarbons, such as for instance di- and trichloroethylene, chloroform, methylene chloride, mercaptan, and propane.

Examples of further suitable polymerisation adjuvants are to be found in H. Kainer, *Polyvinylchlorid und Vinylchlorid-Mischpolymeride*, 1965 Edition, pages 13 to 34.

The polymerisation is carried out at temperatures of 30 to 80, preferably 40 to 65, and in particular 45 to 60°C, in which process polymerisation may take place optionally with refluxing, use of 2 or more stirring speeds and/or temperature steps. The pH-value of the polymerisation bath should be between 2 and about 9, preferably between 3 and 7.

During the polymerisation one or more of the following substances can be added, optionally with the filling volume of the polymerisation vessel being kept constant: water, aqueous solutions, monomers, catalysts, cocatalysts, further polymerisation adjuvants, such as for instance control agents, buffer substances, emulsifiers, suspending agents.

Polymerides prepared according to the invention can be freed of residual monomers, in particular vinyl chloride, according to known processes both in aqueous dispersion and as water-damp cakes or in powdered moist or dry condition.

- 5 The reconditioning of an aqueous polymeride suspension to a dry powder likewise takes place according to known methods, for instance by decanting the bulk of the aqueous phase in a decanting centrifuge and drying the thus obtained water-damp cake in a pneumatic-conveyor drier or a fluidising drier.
- 10 Thus obtained powdered polymerides, like polymerides of vinyl chloride common up to now, can be thermoplastically processed for instance by means of extrusion, injection moulding or calendering.

The process according to the invention makes a polymerisation with a very balanced
15 heat production possible, as a result of which the cooling capacity of the apparatuses is used to optimum effect and as a result high space-time yields can be obtained. At the same time a considerably lower formation of wall coatings in the polymerisation reactors is determined than in the case of comparable processes according to the state of the art. As a result of this lower wall coating formation the obtained
20 polymerides contain fewer contaminations, in particular coarse components and particles, which are hard to break up thermoplastically and after processing give inhomogeneities known as "fish-eyes" or "dots". The polymerides obtained according to the new process are suitable for all common heat stabilisations. In particular in the case of stabilisation with lead-containing compounds a lower tendency to discolour is
25 established.

The following examples serve to further elucidate the invention. For comparison with processes according to the state of the art a series of comparative experiments was carried out which hereinafter are characterised with capitals and which for a better
30 overall view have been compiled in a table together with the results of examples according to the invention characterised with numbers.

For characterising the balanced heating pattern during the polymerisation the following are indicated:

The running time of a polymerisation batch in hours until the conversion indicated in the text for each Example is reached (86 to 90% except for Comparative experiment D).

The maximum difference in °C between the internal temperature of the polymerisation vessel and the temperature of the cooling jacket = ΔT_{MAX} . The larger this difference, the more heat is eliminated via the cooling medium. This quantity is a measure of the maximum dissipation of heat.

The time in hours t during which for a polymerisation batch there is operation with maximum elimination of heat. This number is a measure of the evenness of the polymerisation.

After each polymerisation batch the reactor is cleaned of loosely adhering suspension residues with a water jet emerging under a pressure of 6 bar. After 3 batches and cleanings with pressurised water each the reactor and the installations (stirrers, etc.) are freed of the coatings which stick and cannot be removed with pressurised water, and these are weighed. The coating amount was only determined in Comparative experiments B and C as well as in Example 1 and is indicated in g in the Table below.

The K-value is measured in accordance with DIN 53 726, with cyclohexanone being used as solvent.

For all Examples and Comparative experiments detailed below an autoclave of chrome-nickel steel (V2A-Stahl) is used which has a content of 400 l and is equipped with stirrers, power interrupters, and temperature controlling equipment.

Comparative experiment A

Into the autoclave described above in greater detail are charged 220 l of fully desalinated water wherein 58 g of a partially acetylated polyvinyl alcohol and 42 g of

a methyl cellulose are dissolved, together with 256 g of a sorbitan fatty acid ester and 82 g of bis(4-t-butyl-cyclohexyl)-peroxydicarbonate. After the closing of the autoclave the air present therein is removed by means of evacuation and 135 l of vinyl chloride are dosed. After switching on of the stirrer the contents of the kettle are heated and the polymerisation is carried out at 55°C; a vinyl chloride pressure of 910 kPa is set. When the pressure has fallen to 760 kPa, which corresponds to a conversion of 86%, the polymerisation is broken off and the suspension is recovered. Obtained is a product having a K-value of 70, which is suitable for thermoplastic processing, together with conventional plasticisers. The values determined during the polymerisation are listed in the Table below.

Comparative experiment B (analogous to DE-AS 19 15 386)

The process is as in Comparative experiment A; however, as catalysts 34 g of diisopropyl-peroxydicarbonate and 15 g of acetyl-cyclohexylsulfonyl peroxide are used.

After three batches, with the polymerisation autoclave being cleaned in between with pressurised water as described above, in total 410 g of a very hard coating are removed from the reactor from the wall, power interrupter, and stirrer.

Comparative experiment C (analogous to DE-AS 21 39 680)

The process is as in Comparative experiment A; however, as catalysts 60 g of dicetyl-peroxydicarbonate and 18 g of acetyl-cyclohexylsulfonyl peroxide are used. After three batches with cleaning in between 172 g of sticky coatings are removed from the reactor, including stirrer and power interrupter.

Comparative experiment D

The process is as in Comparative experiment A; however, as catalyst 84 g of cumyl perneodecanoate without further additions are used. The polymerisation proceeds slowly. After 12 hours the otherwise common final pressure was not yet reached. The polymerisation was broken off at a pressure of 890 kPa. For measured values see the Table.

Example 1

The process is as in Comparative experiment A; however, as activators 51 g of bis(4-t-butylcyclohexyl)-peroxydicarbonate and 35 g of cumyl perneodecanoate are used. After three batches with cleaning in between 64 g of sticky coating is removed from the inside wall of the reactor, the stirrer, and the power interruptor.

Example 2

Into the autoclave described above in greater detail are charged 208 l of fully desalinated water wherein 147 g of a partially acetylated polyvinyl alcohol are dissolved, together with 136 g of a water-insoluble, partially acetylated polyvinyl alcohol, 39 g of o,o'-dimethyl-benzoyl peroxide, 42 g of bis(4-t-butylcyclohexyl)-peroxydicarbonate, and 36 g of cumyl perneodecanoate.

After the closing of the autoclave the air present therein is removed by means of evacuation and 138 l of vinyl chloride and 18 l of vinyl acetate are dosed. After switching on of the stirrer the contents of the kettle are heated and the polymerisation is carried out at 61°C; a vinyl chloride pressure of 1,010 kPa is set. When the pressure has fallen to 610 kPa, which corresponds to a conversion of 90%, the polymerisation is ended and the suspension is recovered. Obtained is a product having a K-value of 60, which contains 10 wt.%, calculated on polymer, of polymerised vinylacetate units and which is suitable for thermoplastic processing without plasticisers. The values determined during the polymerisation are listed in the Table below.

Example 3

Into the autoclave described above in greater detail are charged 210 l of fully desalinated water wherein 78 g of a partially acetylated polyvinyl alcohol and 270 g of a methyl cellulose are dissolved, together with 27 g of a sorbitan fatty acid ester, 35 g of o,o'-dimethylbenzoyl peroxide, and 39 g of cumyl perneodecanoate. After the closing of the autoclave the air present therein is removed by means of evacuation and 135 l of vinyl chloride are dosed. After switching on of the stirrer the contents of the kettle are heated and the polymerisation is carried out at 60°C; a vinyl chloride pressure of 1,030 kPa is set. When the pressure has fallen to 610 kPa, which

corresponds to a conversion of 90%, the polymerisation is broken off and the suspension is recovered. Obtained is a product having a K-value of 65, which is suitable for thermoplastic processing with the addition of conventional plasticisers.

- 5 In the following Table the specifications in per cent are to be taken as weight percentages, calculated on the monomer or monomers mixture used.

TABLE

Comp. exper./ Ex.	Catalysts used	Running time (h)	ΔT_{MAX} (°C)	t (h)	Amt. of coating after 3 batches (g)
A	0.066% bis(4-t-butylcyclohexyl)-peroxydicarbonate	6.0	35.5	0	-
B	0.027% di-isopropyl peroxydicarbonate 0.012% acetylcyclohexyl sulfonyl peroxide	5.9	25.5	2.5	410
C	0.048% dicetyl peroxydicarbonate 0.014% acetyl cyclohexyl sulfonyl peroxide	6.0	26.5	3.2	172
D	0.067% cumyl perneodecanoate	>12	20.5	1.5	-
1	0.041% bis(4-t-butylcyclohexyl) peroxydicarbonate 0.028% cumyl perneodecanoate	5.0	28.5	3.5	64
2	0.029% bis(4-t-butylcyclohexyl) peroxydicarbonate *) 0.027% o,o'-dimethylbenzoyl peroxide *) 0.025% cumyl perneodecanoate *)	4.5	34	2.8	-
3	0.028% o,o'-dimethylbenzoyl peroxide 0.031% cumyl perneodecanoate	5.5	31	3.2	-

*) calculated on monomers mixture

Claims

1. Process for the preparation of homo-, co- or graft copolymerides of vinyl chloride by means of polymerisation of vinyl chloride alone or with up to 30 wt.%, calculated on used vinyl chloride, of at least one monomer which is copolymerisable with vinyl chloride and/or of at least one polymer which is graft-copolymerisable with vinyl chloride, in aqueous suspension or in mass at 30 to 80°C in the presence of at least two oil-soluble, radical-forming peroxide groups-containing catalysts, as well as optionally in the presence of suspending agents and further added substances, characterised in that as catalysts are used 0.001 to 0.5 wt.%, calculated on used monomers, of cumyl perneodecanoate and 0.001 to 0.5 wt.%, calculated on used monomers, of at least one further peroxide groups-containing catalyst known for the polymerisation of vinyl chloride, which has a 1-hour half-life temperature of 50 to about 100°C.
2. A process according to claim 1, characterised in that the overall amount of used catalysts is 0.01 to 0.5 wt.%, calculated on used monomers.
3. A process according to claim 1 or 2, characterised in that polymerisation takes place at a temperature of 40 to 65°C.
4. A process according to any one of claims 1 to 3, characterised in that polymerisation takes place in the presence of 0.01 to 0.1 wt.%, calculated on used monomers, of cumyl perneodecanoate.
5. A process according to any one of claims 1 to 4, characterised in that polymerisation takes place in the presence of 0.01 to 0.1 wt.%, calculated on used monomers, of at least one catalyst known for the polymerisation of vinyl chloride, except for cumyl perneodecanoate, which has a 1-hour-half-life temperature of 50 to 100°C.

6. A process according to any one of claims 1 to 5, characterised in that polymerisation takes place in the presence of cumyl perneodecanoate and at least one peroxydicarbonate which contains 14 to about 40 C-atoms.
- 5 7. A process according to any one of claims 1 to 6, characterised in that polymerisation takes place in the presence of cumyl perneodecanoate and bis-(4-t-butyl-cyclohexyl) peroxydicarbonate.